Structure and Dynamics of Levitated Liquids

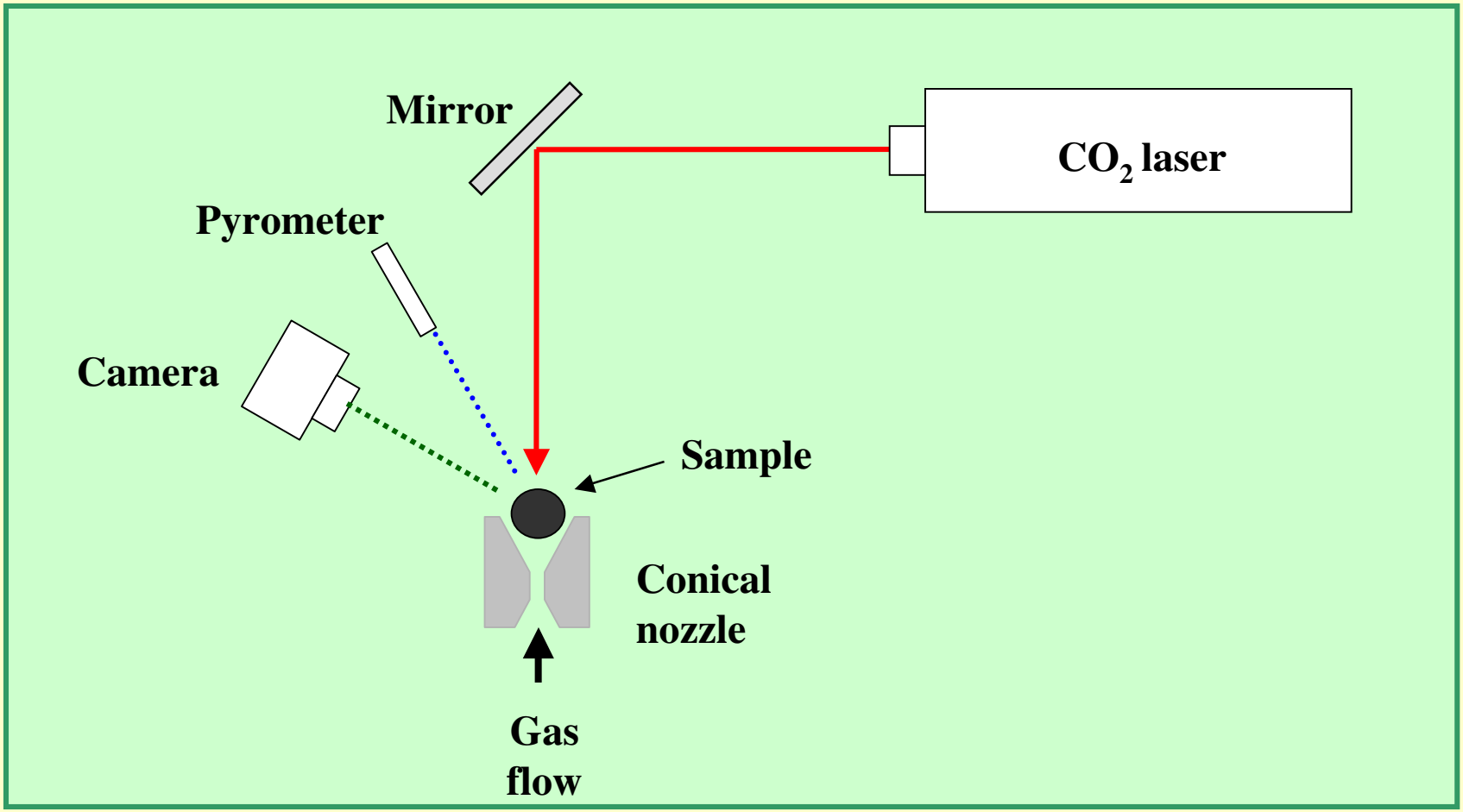
David L. Price

"Neutron Research at NIST"

A symposium honoring Mike Rowe and Jack Rush

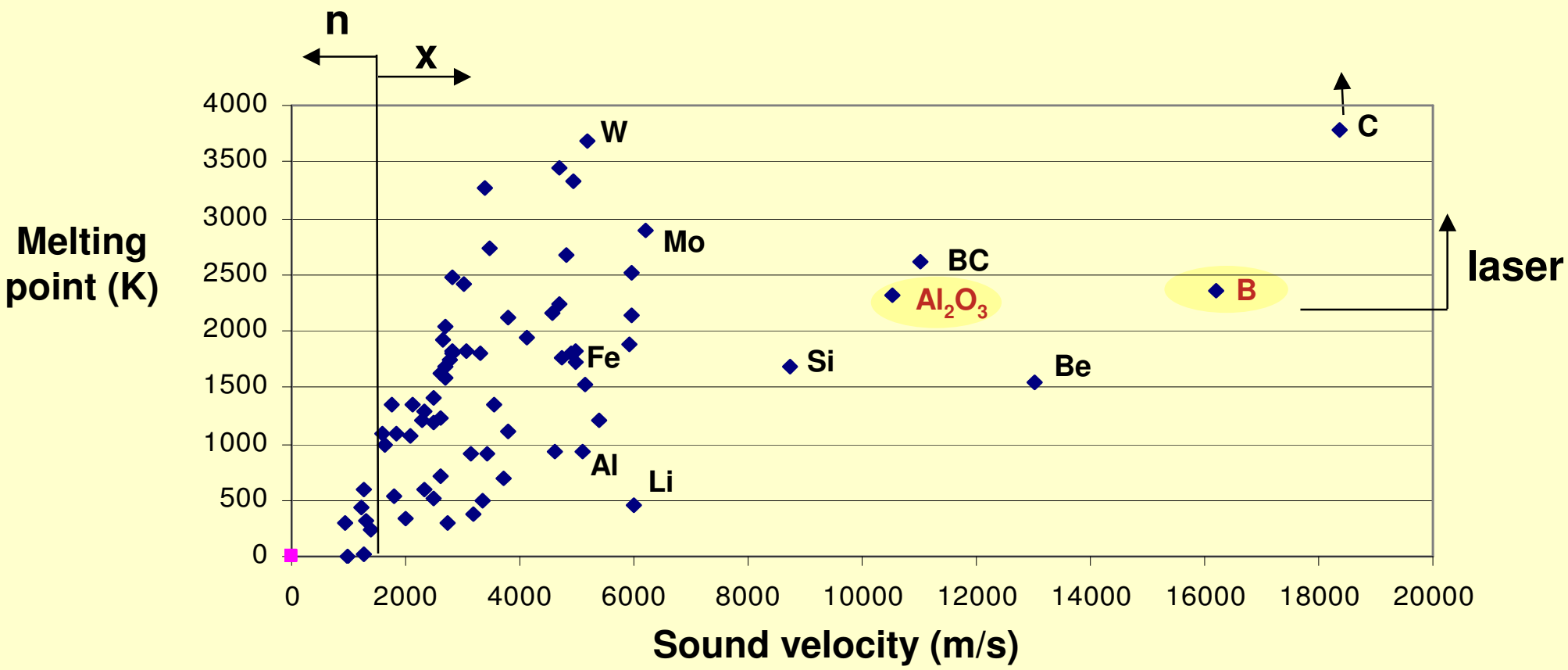
September 9, 2005 - Rockville, Maryland

Aerodynamic levitation with laser heating



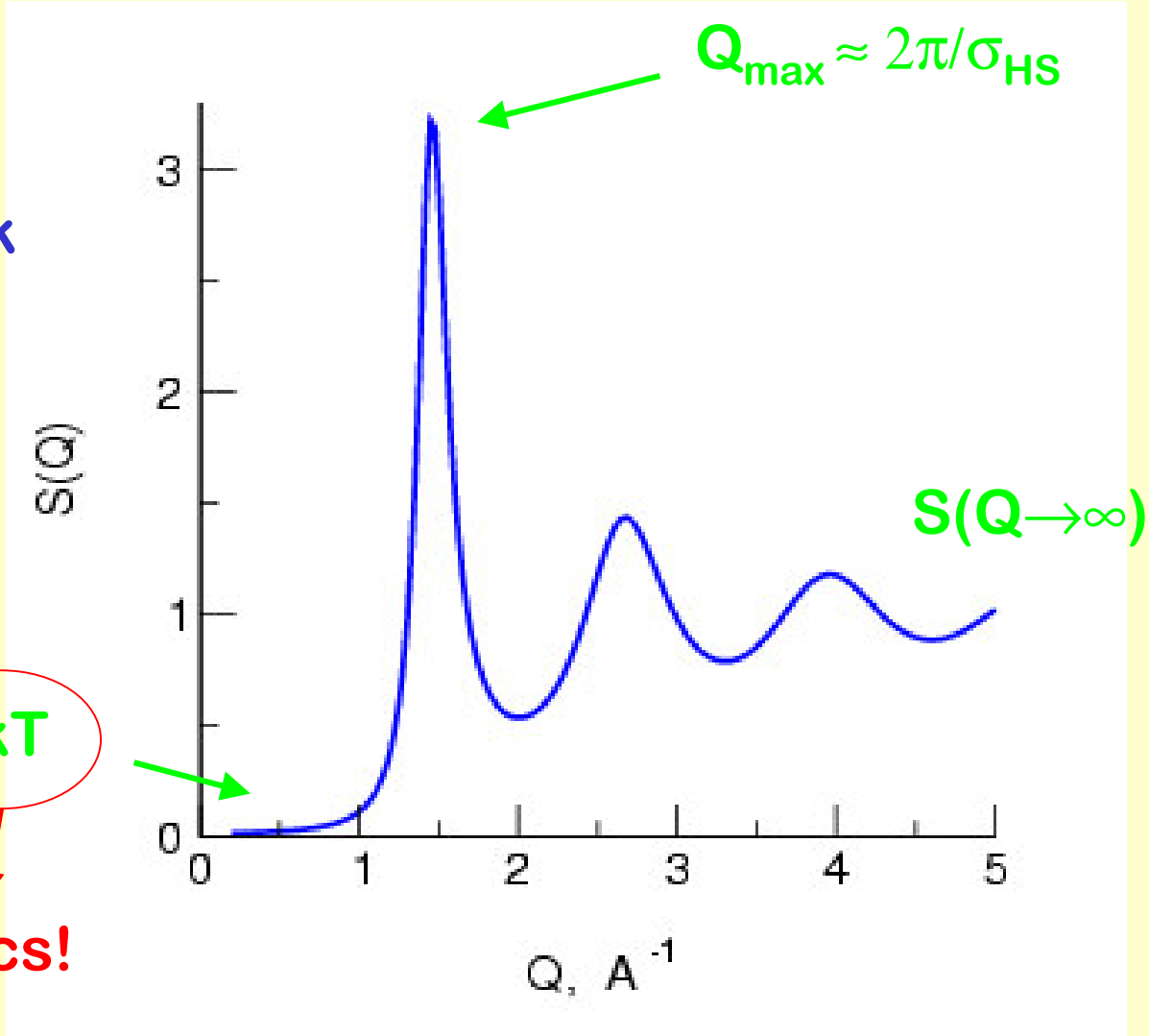
High-Melting Substances

Lindemann criterion: $mv^2_{sound} \propto T_{melt}$



Liquid structure factor

Percus-Yevick equation



$S(Q=0) = \chi\rho\, kT$

Dynamics!

Solid and liquid aluminum oxide

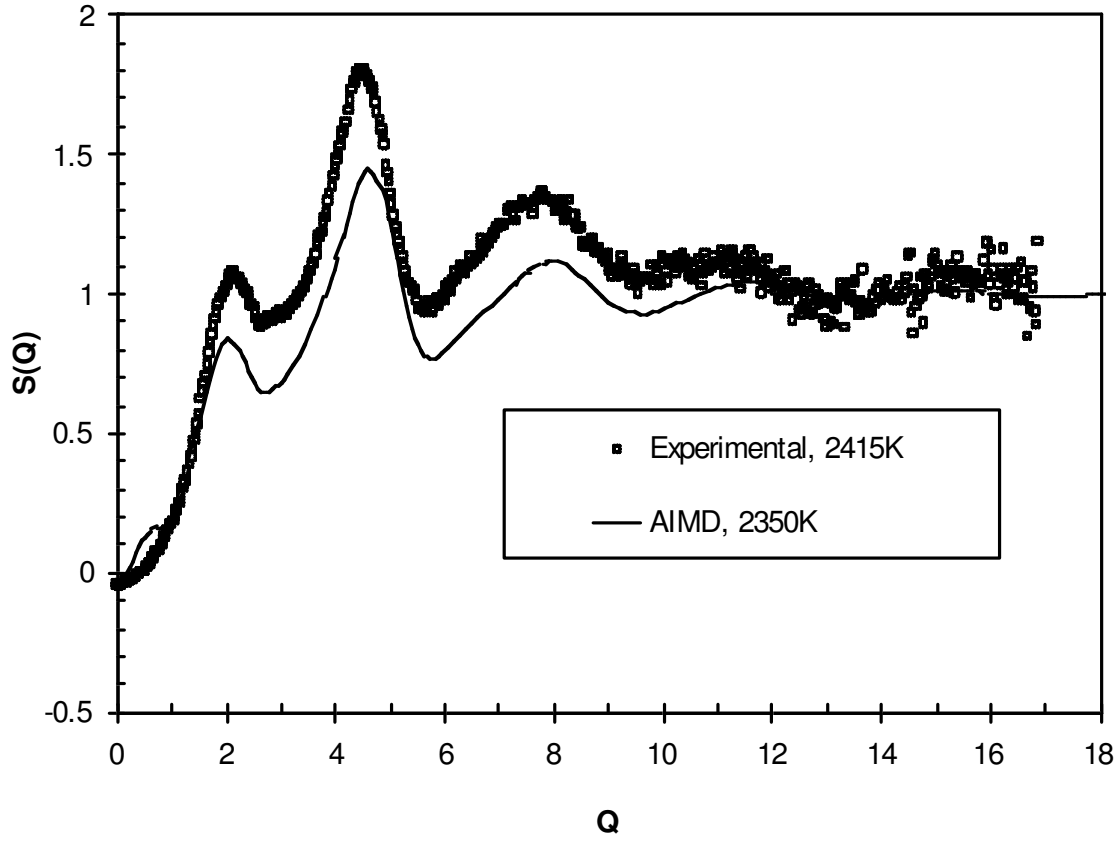
Stable form: α-Al_2O_3: corundum structure
Al in octahedral sites [$C_{Al}(O)=6$]
r(Al-O)=1.91Å
d=3.97 g/cm^3

Metastable form: γ-Al_2O_3: defect spinel structure
Al in octahedral & tetrahedral sites (1:2.3)
r(Al-O)=1.87Å
d~2.8 g/cm^3

Liquid Al_2O_3: T_m=2327K
Al in mostly tetrahedral sites [$C_{Al}(O)=4.5\pm0.5$][1]
Structure unknown: d=2.9 g/cm^3

[1]NMR: Coutures *et al.*, CR (1990); Poe *et al.*, JPC (1992).

XRD results (APS, 2002)compared with MD computer simulation

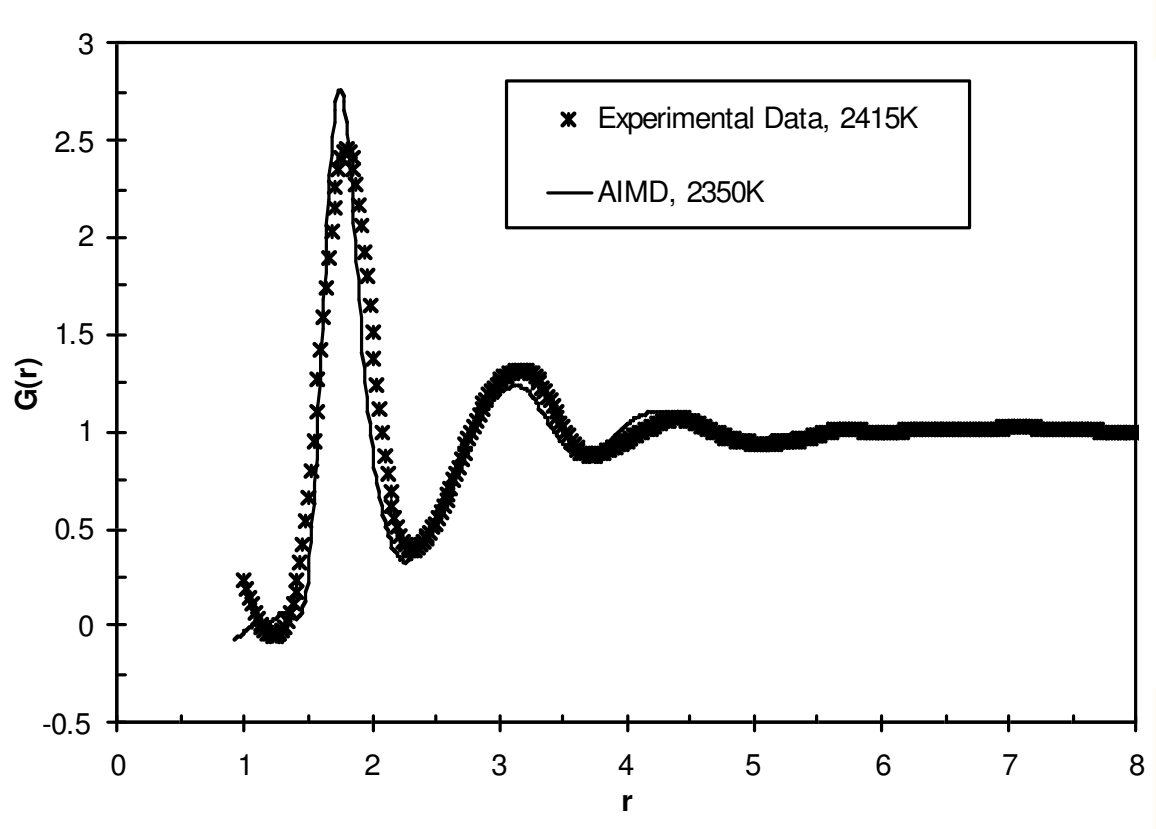


MD simulations performed using an advanced interatomic potential that accounts for instantaneous changes of the electronic structure of individual ions due to variations of their ionic environment.

Includes: charge-charge and dispersion interactions, overlap repulsion and polarization.

[S. Krishnan, L. Hennet, S. Jahn, T. A. Key, P. A. Madden, M.-L. Saboungi and D. L. Price, Chem. Mater. 17, 2662-2666 (2005)]

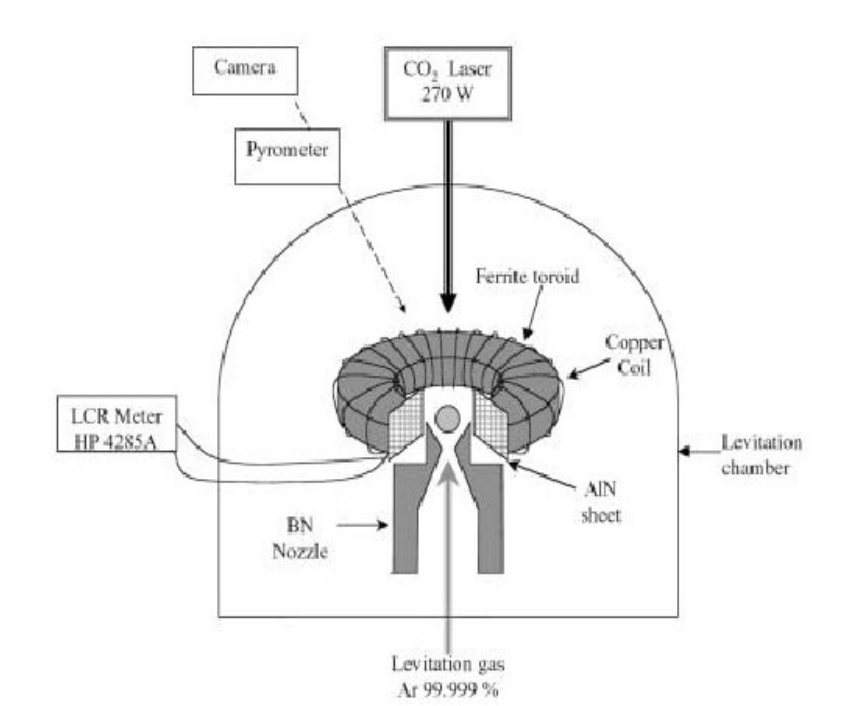
Real-space comparison with MD computer simulation

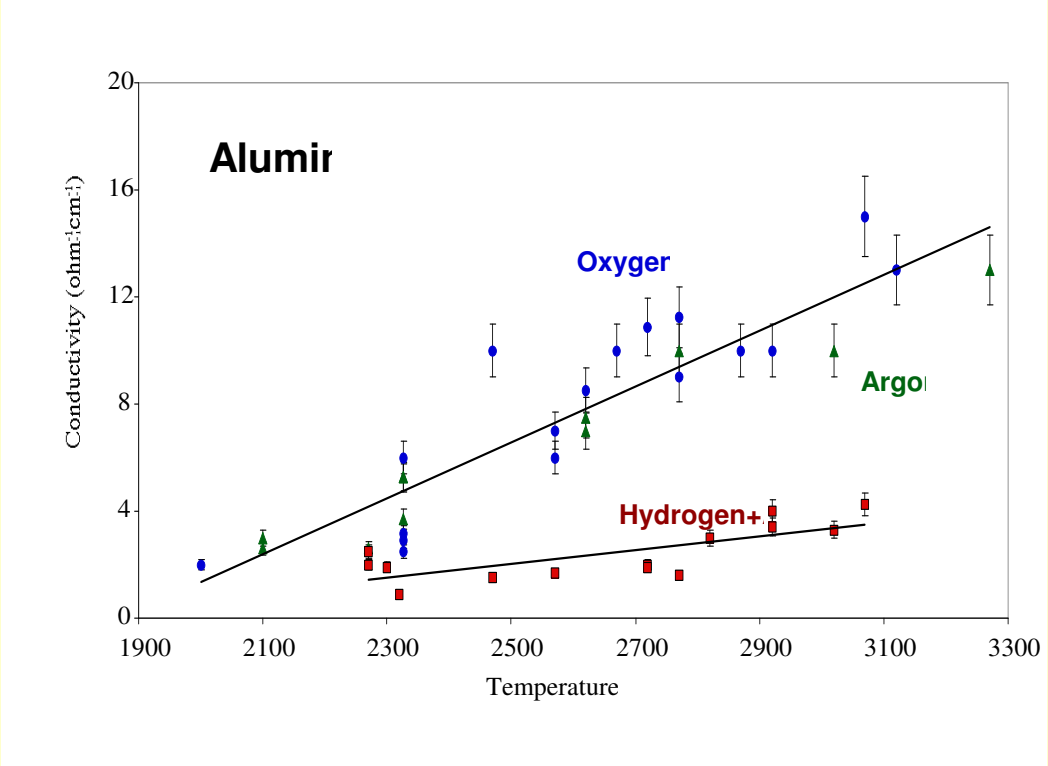


QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Al_2O_3 undergoes an octahedral-tetrahedral transition on melting while in Y_2O_3 an octahedral structure, resembling the hexagonal structure of the high-temperature solid, is preserved

Non-invasive determination of conductivity and permeability





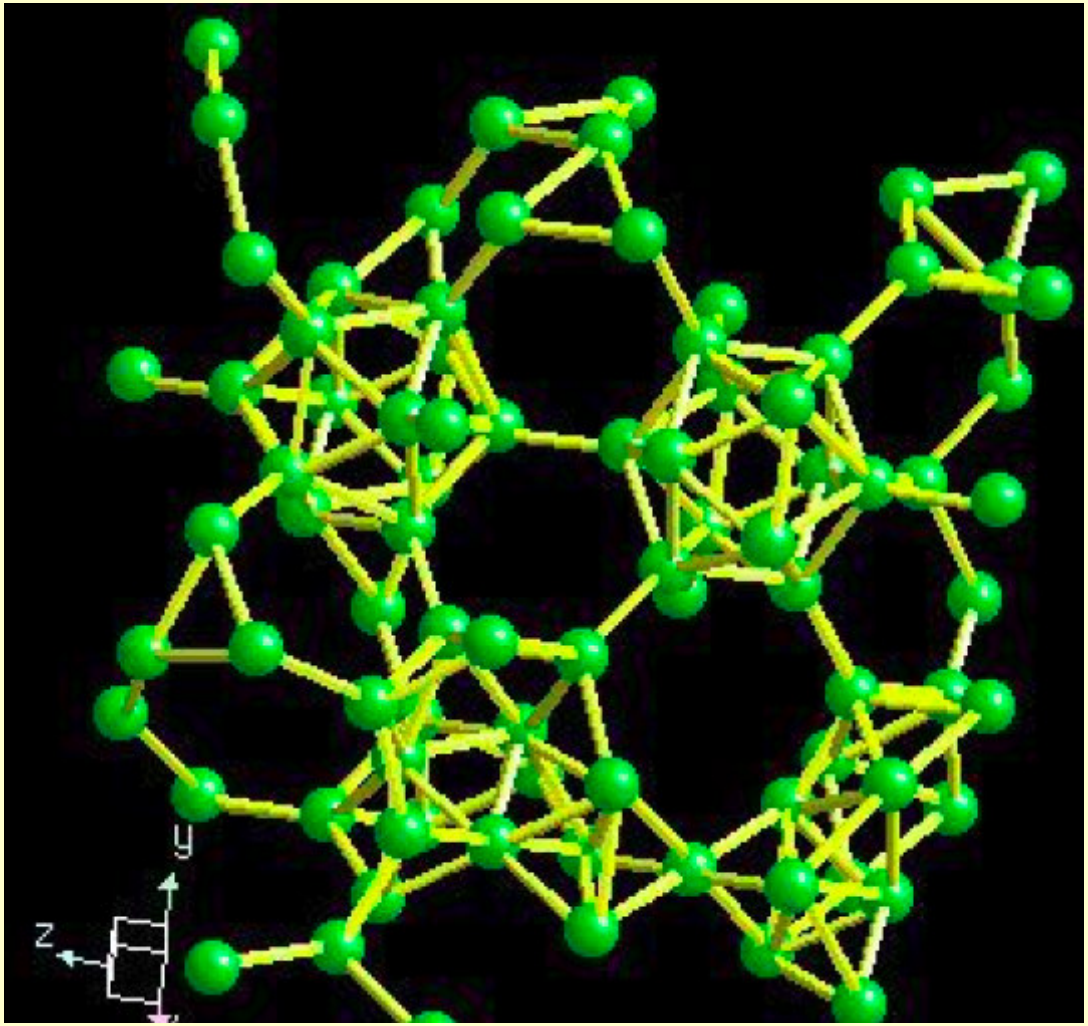
[M.-L. Saboungi et al., JNCS (2002)]

Conduction remains ionic in the liquid , appears to depend on the environment

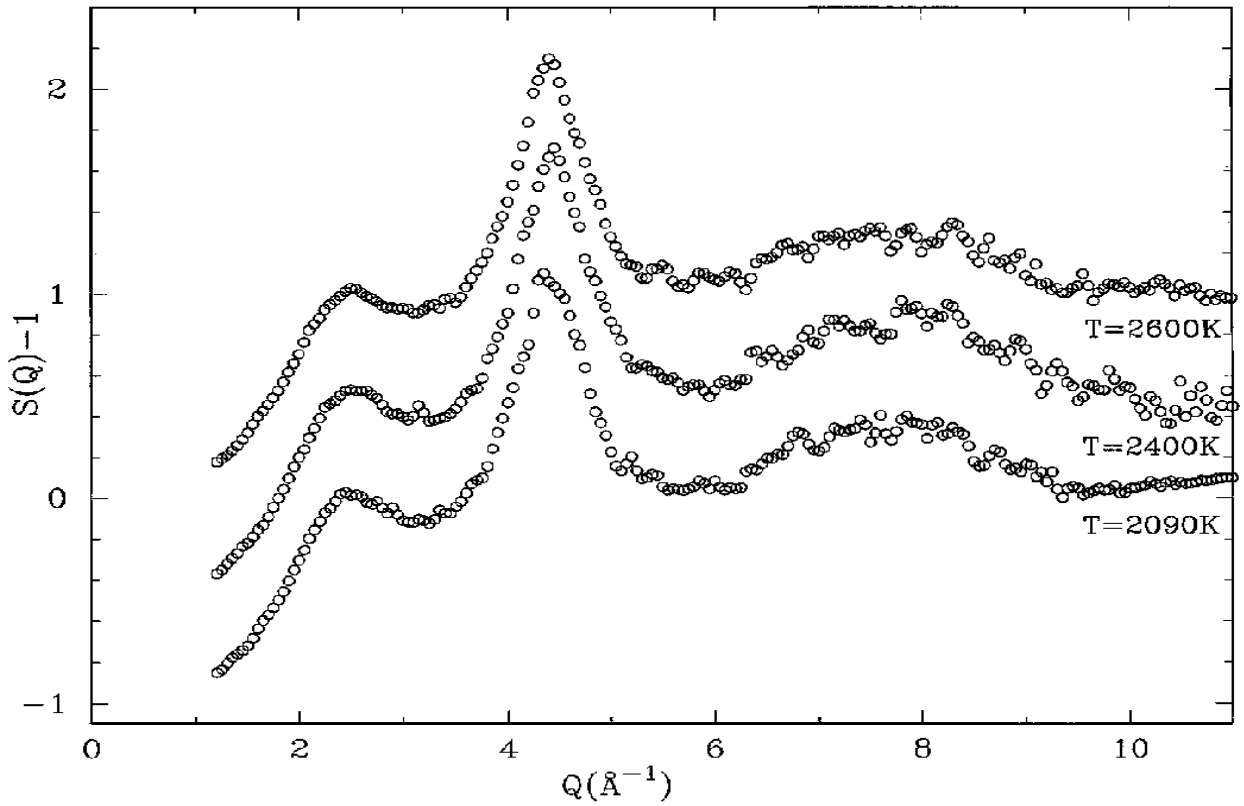
Boron

When solid, the stable crystal structure of boron is rhombohedral

M.p. = 2360 K



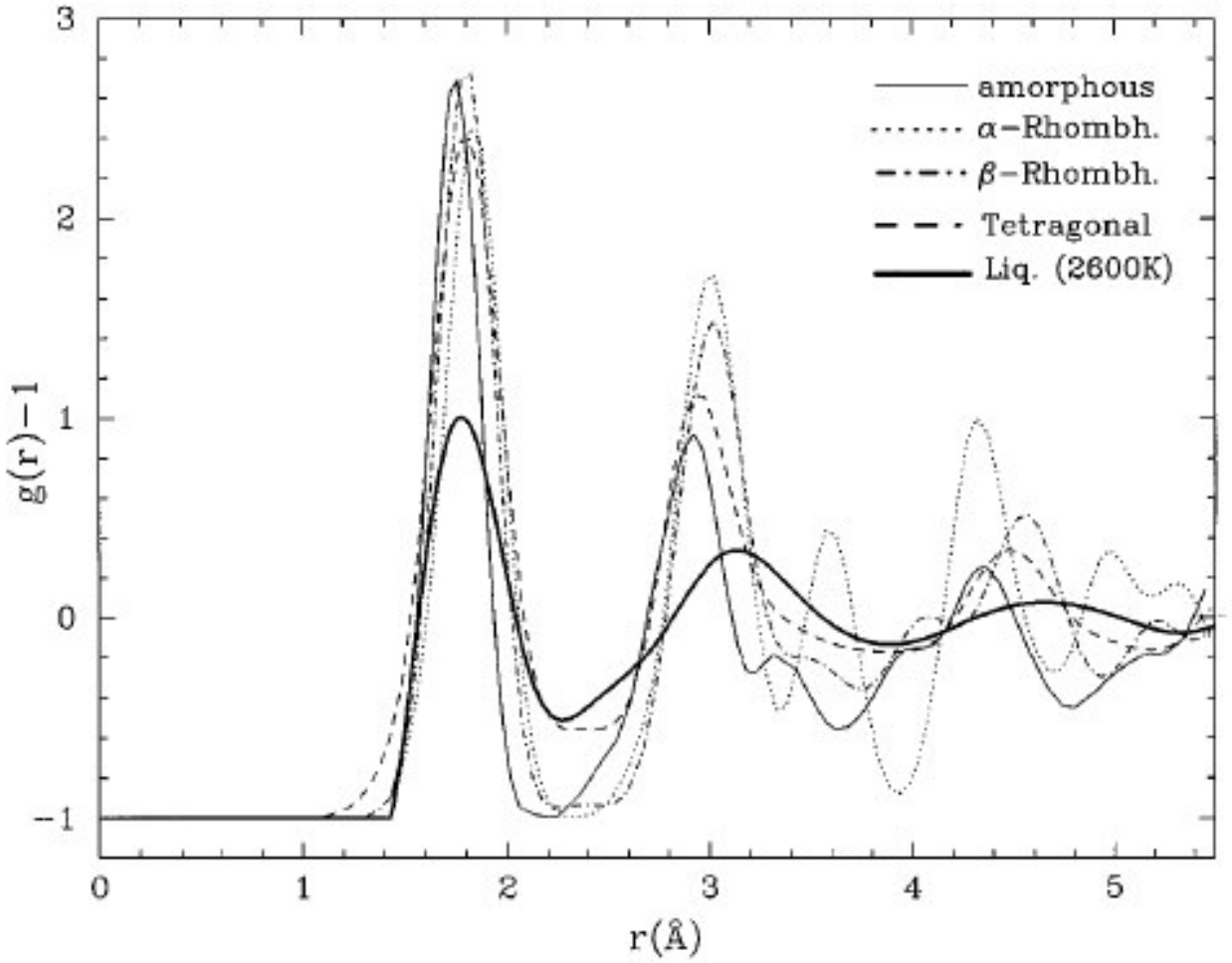
S(Q) of Liquid Boron



Icosahedra/ pentagonal pyramids do not appear To exist in the liquid

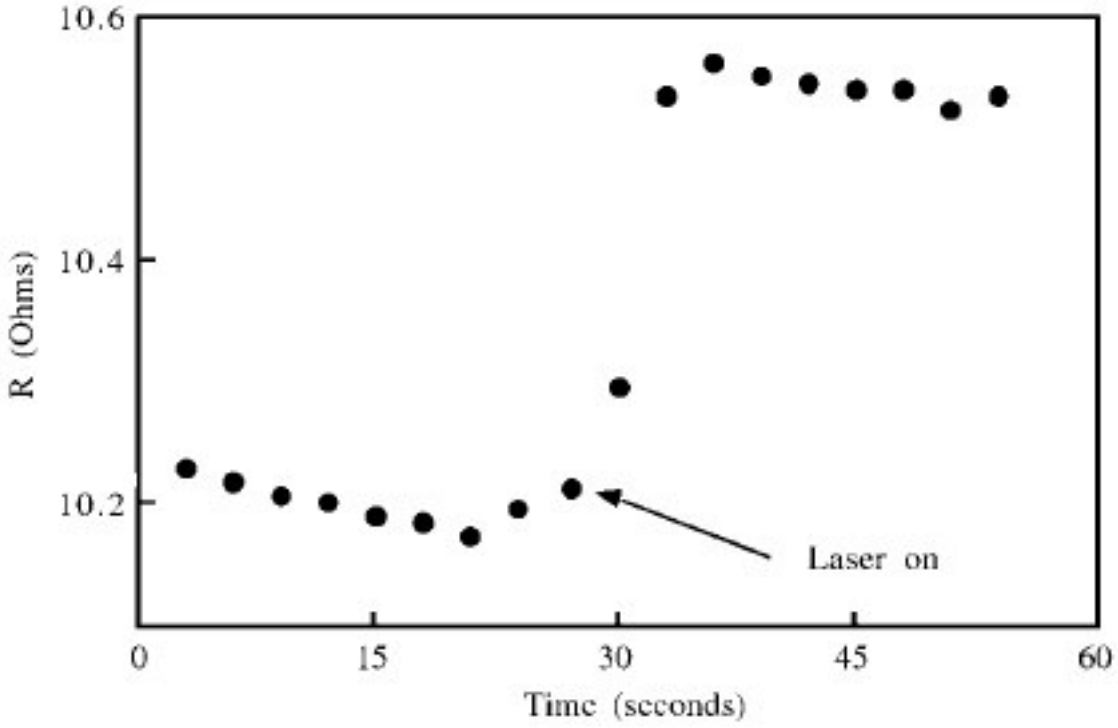
[Krishnan et al., PRL 81, 586 (1998)]

Comparison of the pair distribution function for liquid boron at 2600 K with those for the amorphous, α– and β–rhombohedral, and tetragonal solid forms



Near-neighbor structure essentially unchanged, differences appear at second neighbor and beyond

Change of conductivity of boron on melting

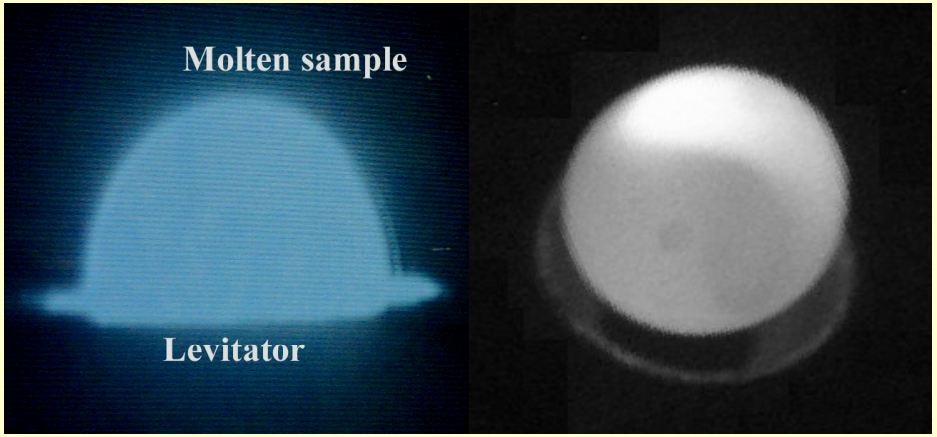


Remains a semiconductor with small increase in conductivity (~500 Ω^{-1} cm^{-1})

B. GLORIEUX[1], M. L. SABOUNGI[1](*) and J. E. ENDERBY[2]

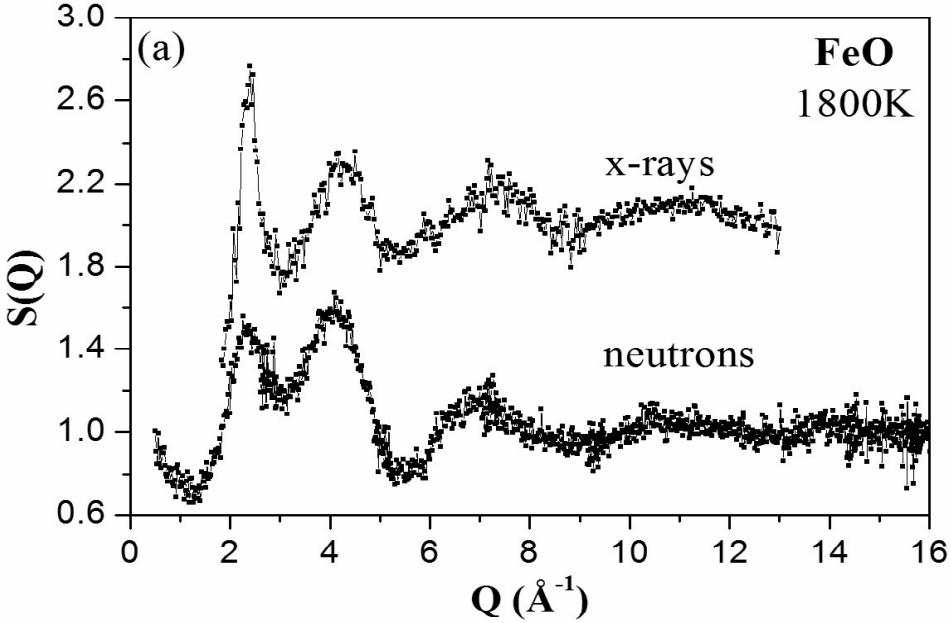
Europhys. Lett., **56** (1), pp. 81–85 (2001)

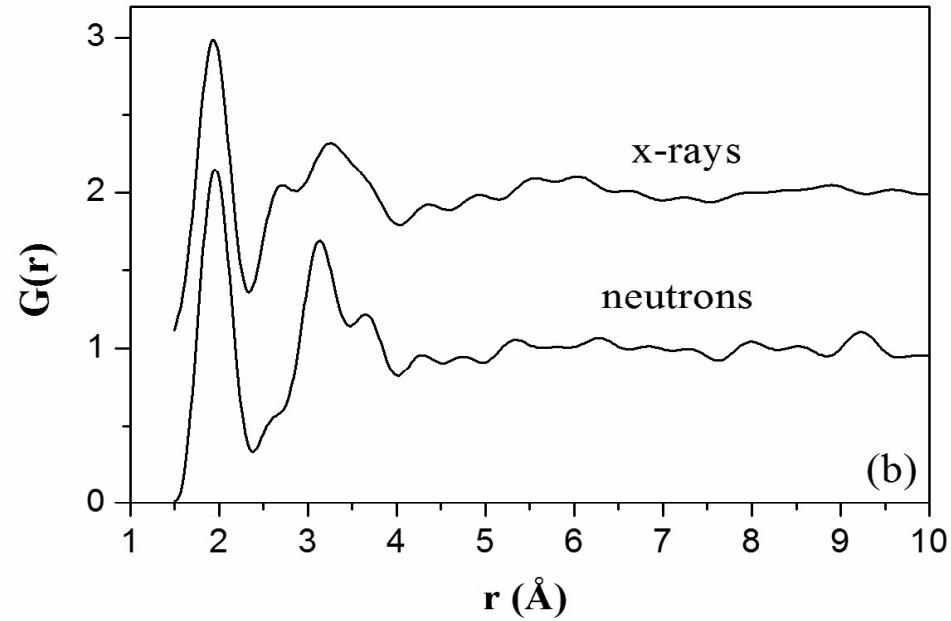
Combination of neutrons and x-rays



$$G_X(r) = 0.36G_{Fe-O} + 0.59G_{Fe-Fe} + 0.05G_{O-O}$$

$$G_N(r) = 0.47G_{Fe-O} + 0.38G_{Fe-Fe} + 0.15G_{O-O}$$



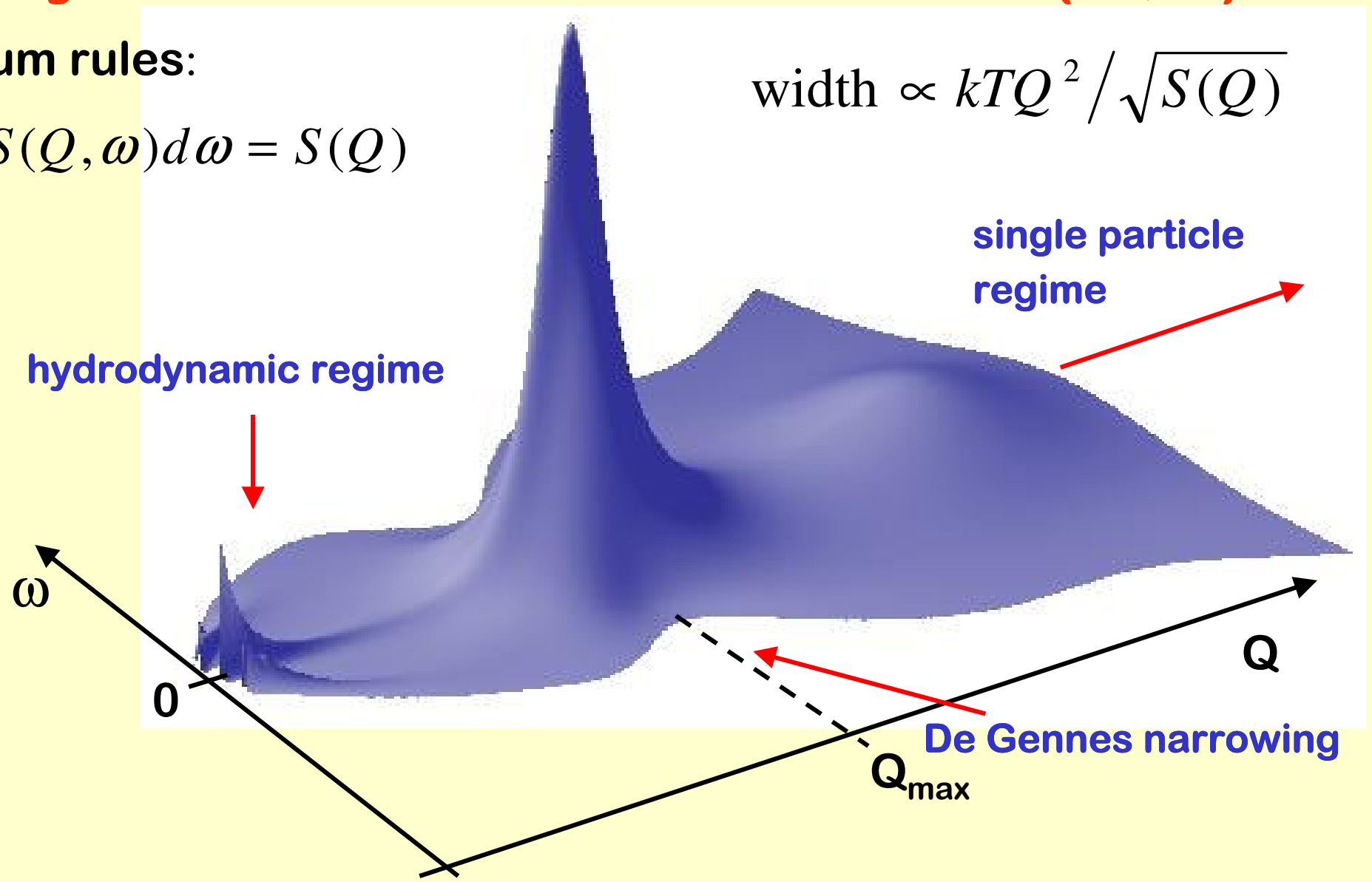


Dynamic structure factor S(Q,ω)

Sum rules:

$$\int S(Q,\omega)d\omega = S(Q)$$

$$\text{width} \propto kTQ^2 \Big/ \sqrt{S(Q)}$$



Thermal-Neutron Time-of-Flight System (TNTOFS)

Installed at CP-5, ANL 1973
(Kleb, Ostrowski,
Price and Rowe)

Reincarnated as LRMECS at
IPNS
1981
- still going strong

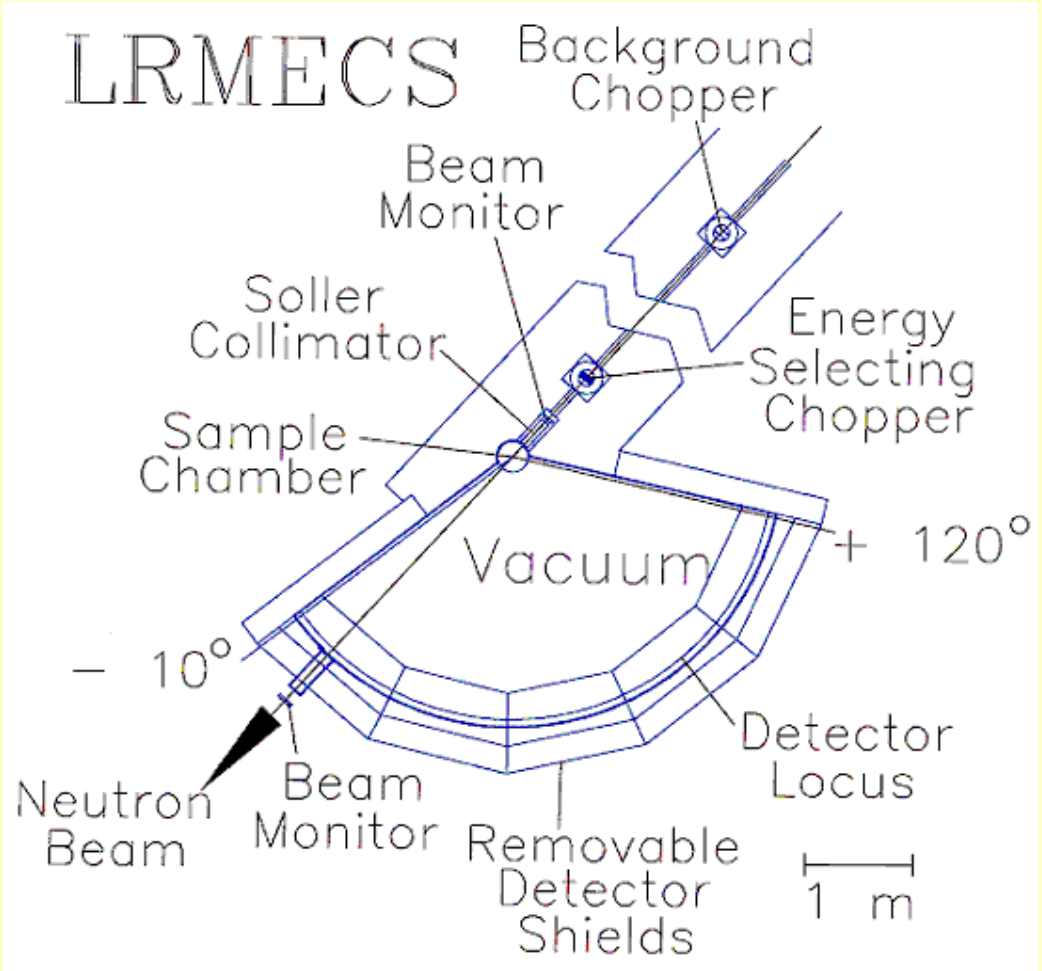
First INS measurement of collective excitations in a liquid metal (Copley & Rowe)

First quantitative measurements of dynamics of a molten salt (Price& Copley)

First measurements of S(Q,ω) in ^{3}He-^{3}He mixtures (Rowe *et al.*)

First measurements of S(Q,ω) in liquid ^{3}He mixtures (Sköld & Pelizzari))

First INS measurements of dynamics of metallic glasses (Rhyne, Moss)



Collective excitations in liquid Rb

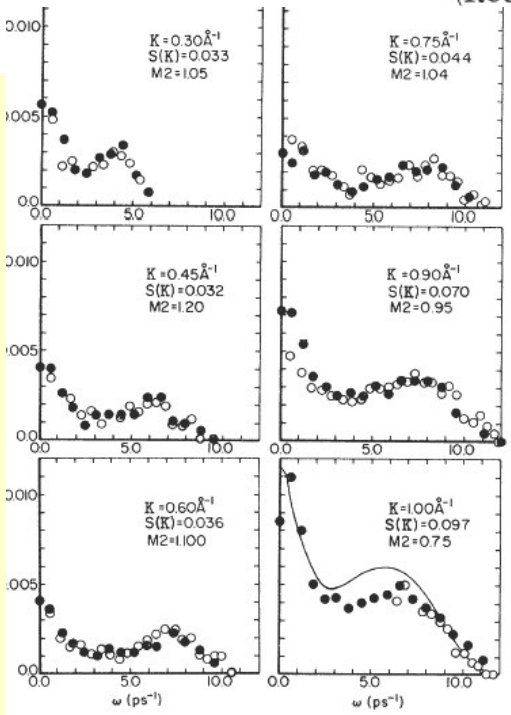
Short-Wavelength Collective Excitations in Liquid Rubidium Observed by Coherent Neutron Scattering*

J. R. D. Copley†
Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439

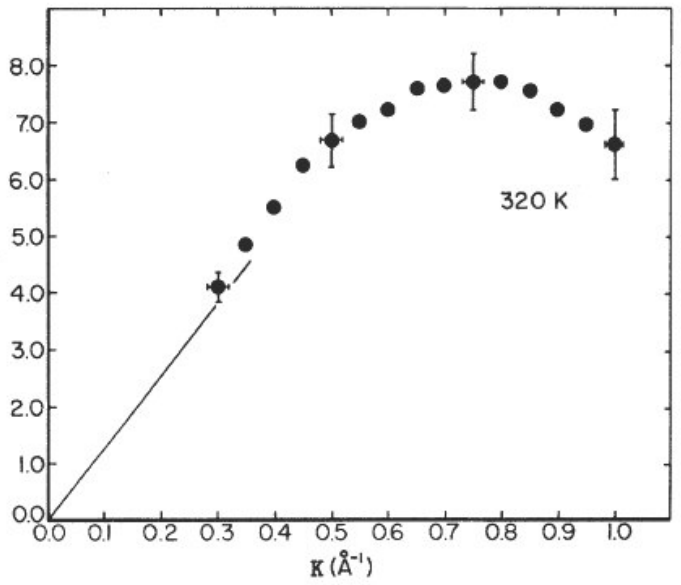
and

J. M. Rowe
Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439, and Institute for Materials Research, National Bureau of Standards, Washington, D.C. 2023

(Received 12 November 1973)

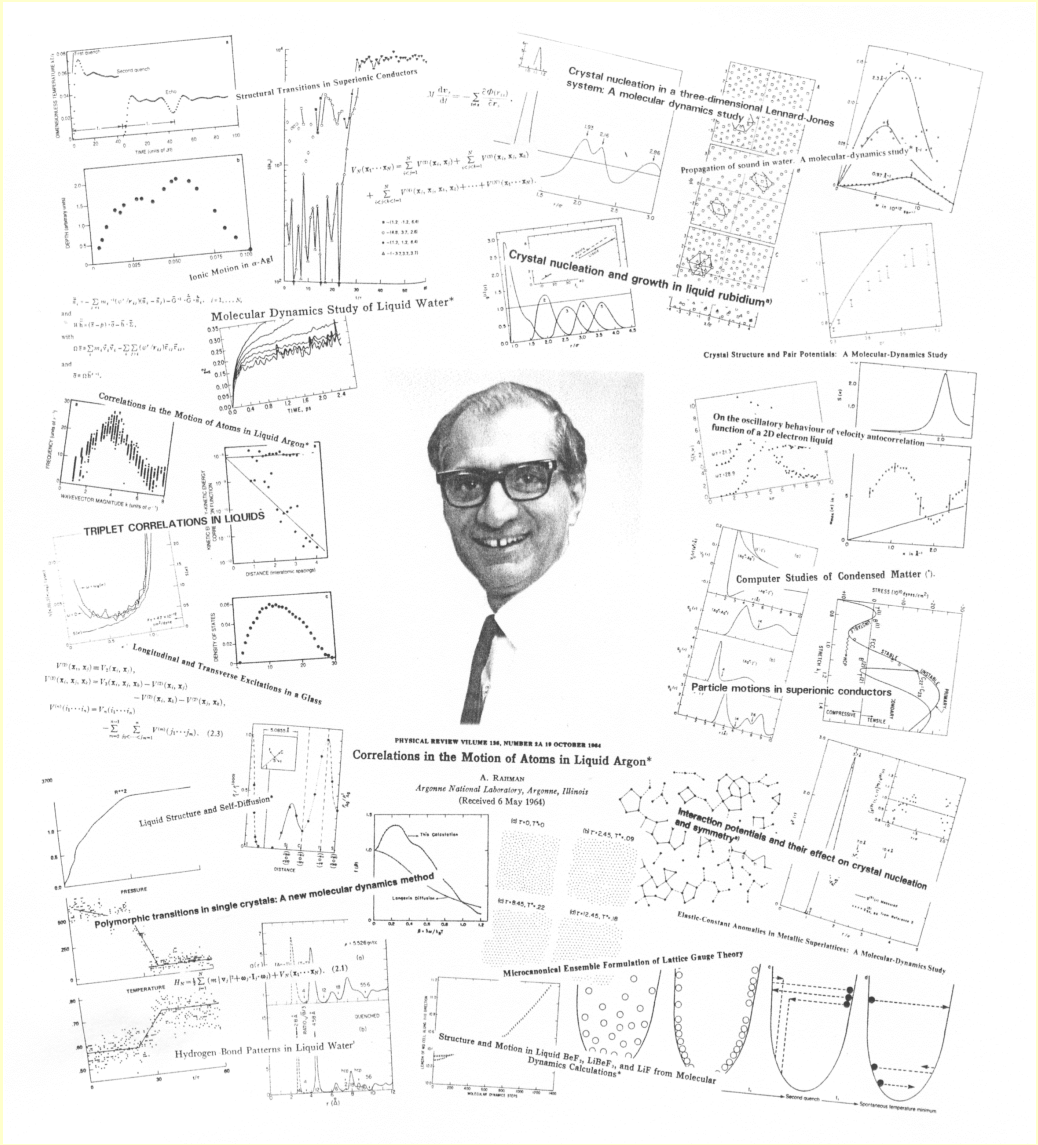


1. Representative results for the symmetrized ring $\tilde{S}(\kappa, \omega)$ of liquid rubidium at constant values



. 2. "Dispersion curve" for liquid rubidium de-

Aneesur Rahman (ANL, 1960-1985)



Rahman Festschrift ~1985

Molecular dynamics of liquid Rb

Propagation of Density Fluctuations in Liquid Rubidium: A Molecular-Dynamics Study*

Aneesur Rahman
Argonne National Laboratory, Argonne, Illinois 60439

1973)

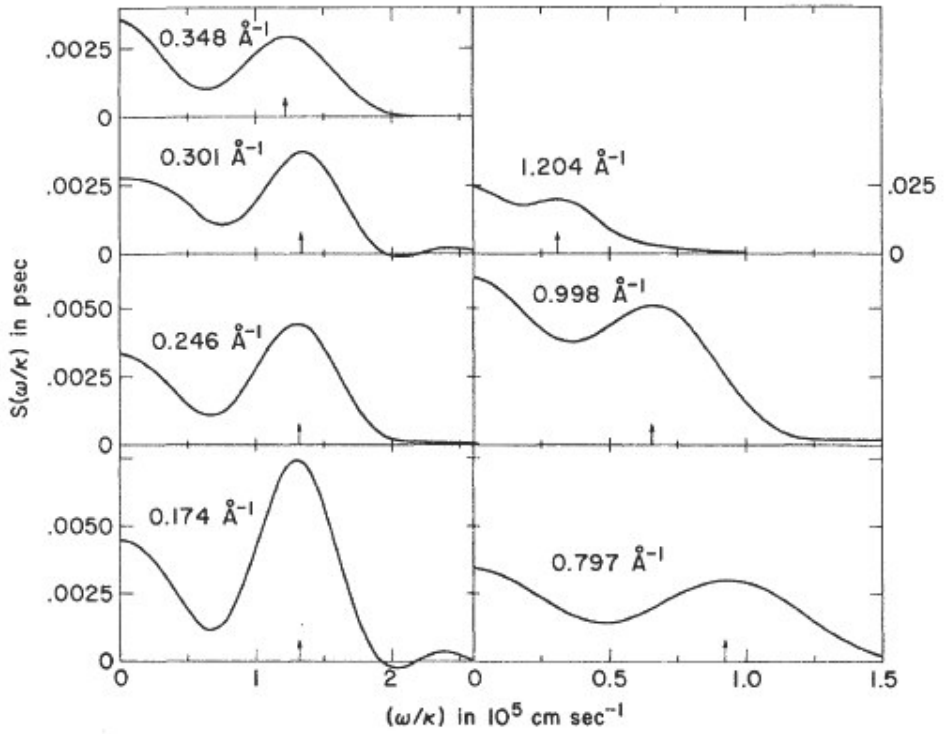
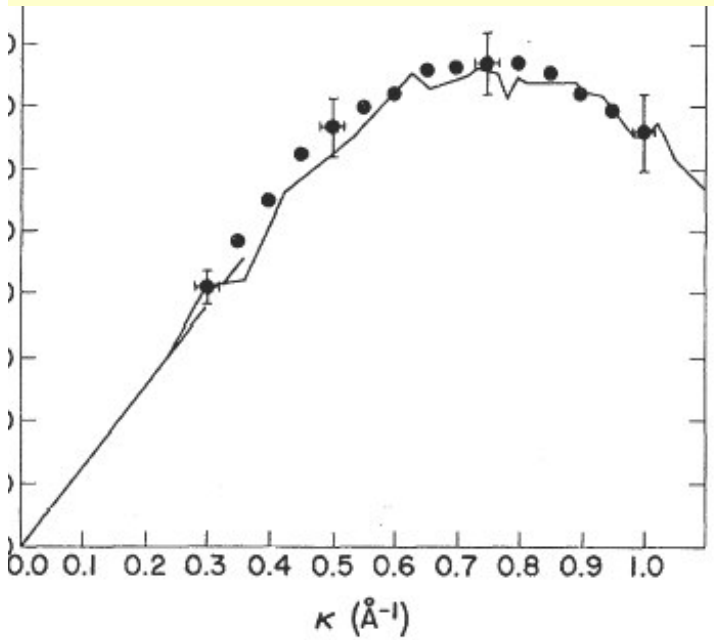


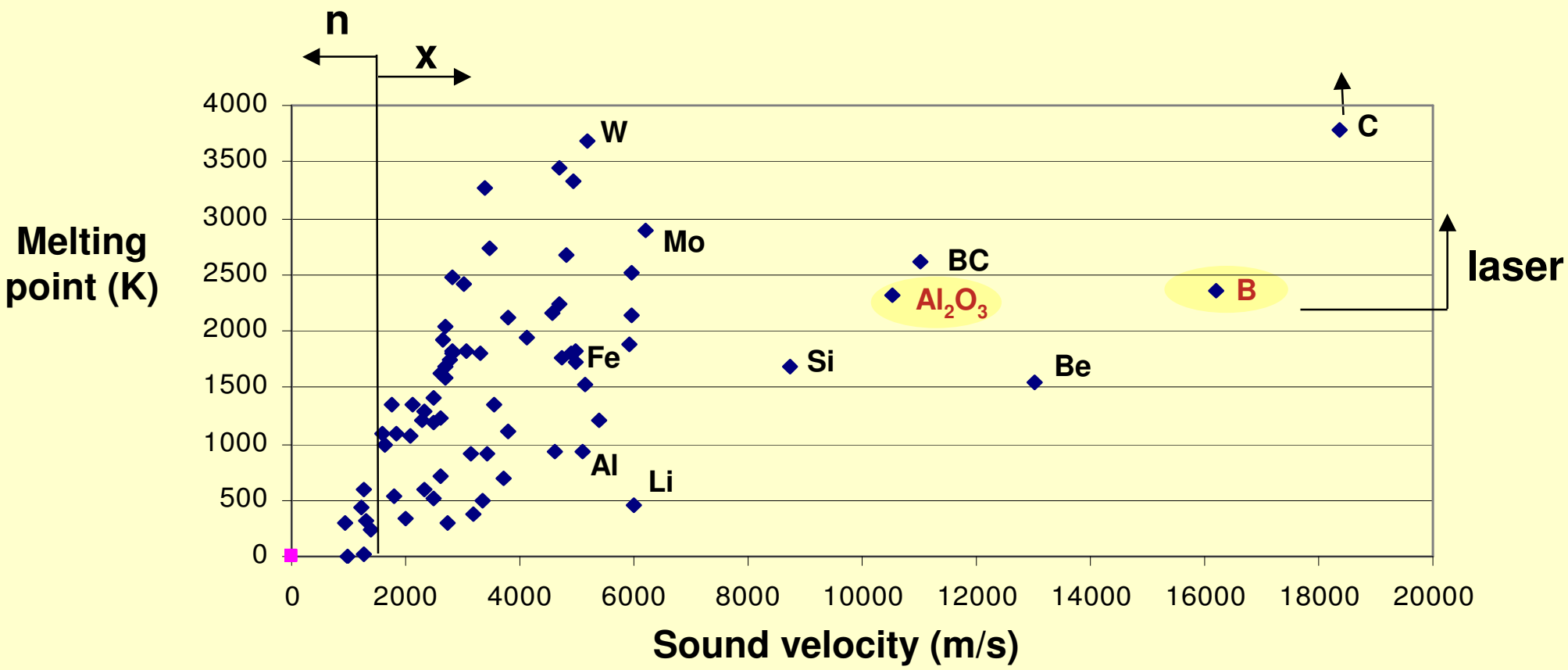
FIG. 1. $S(\kappa,\omega)$ for a few selected values of κ. Note that the abscissa is a velocity. The velocity of sound is



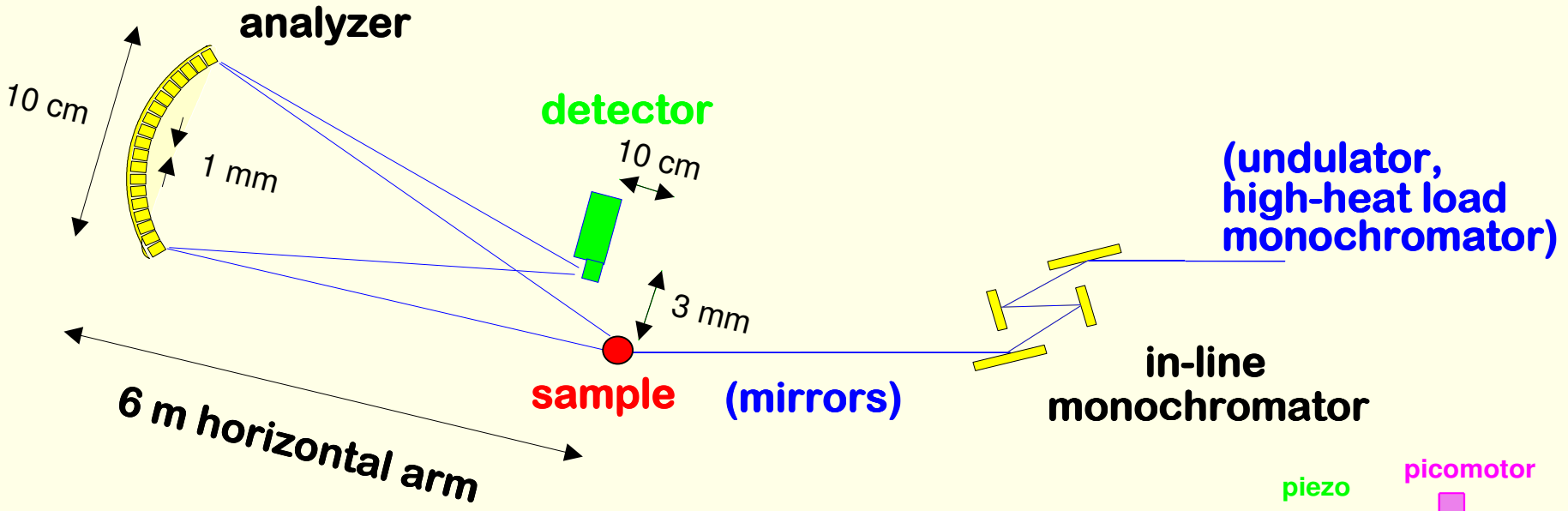
Comparison of MD results with experiment
ω_B is the frequency of the Brillouin peak;

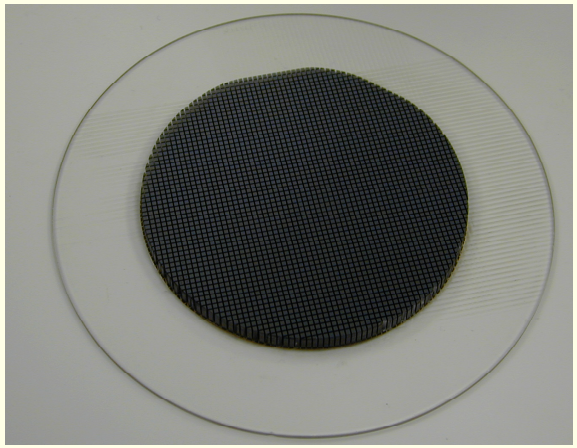
High-Melting Substances

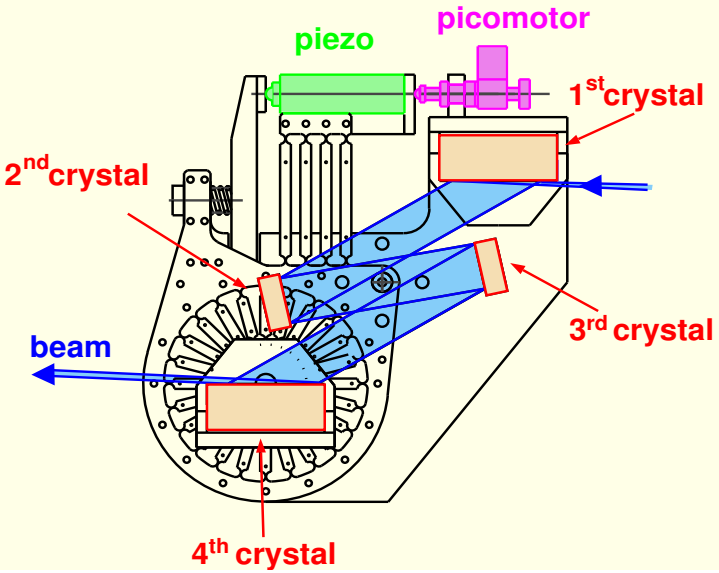
Lindemann criterion: $mv^2_{sound} \propto T_{melt}$



The IXS Spectrometer at 3-ID-C (APS)

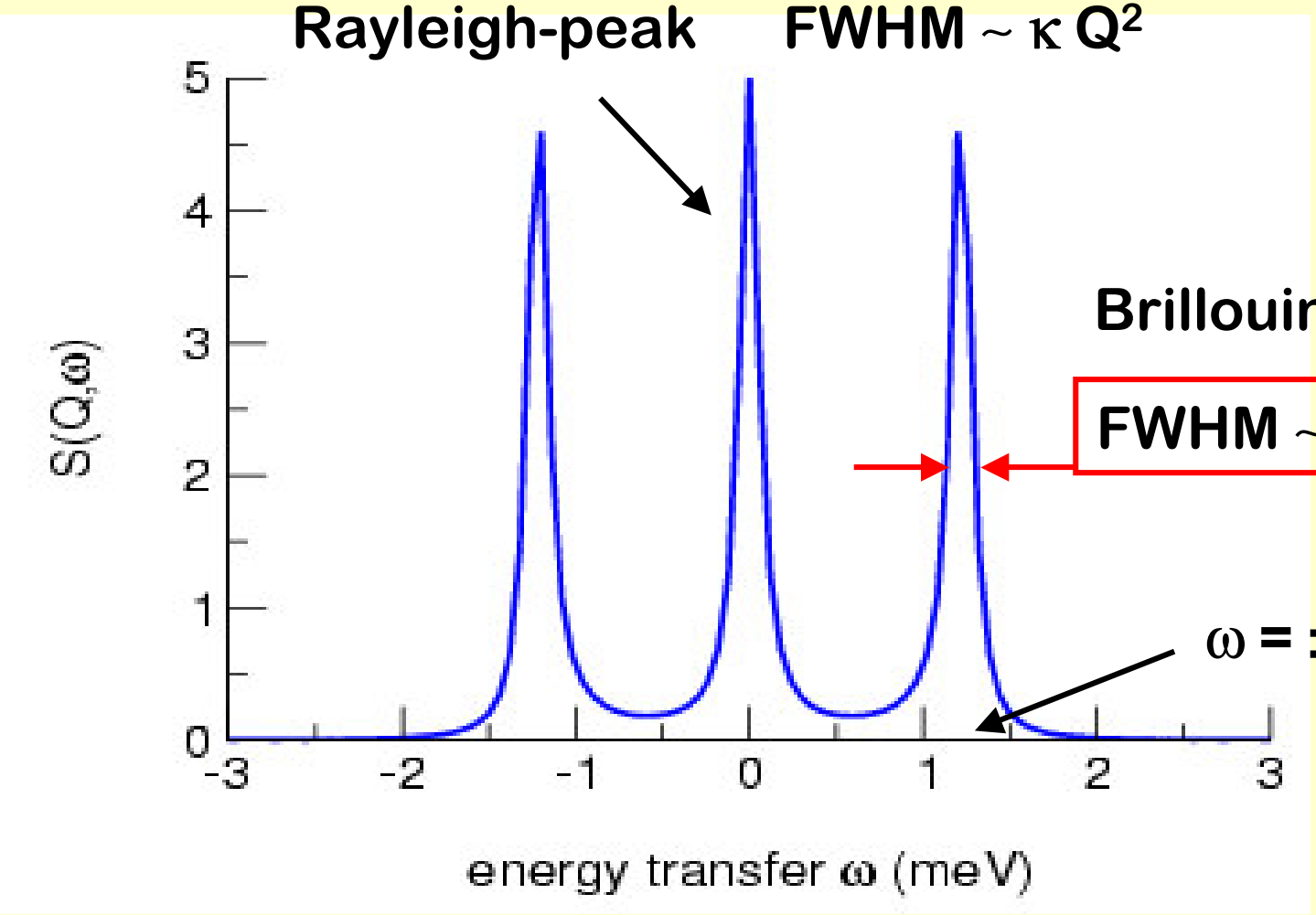




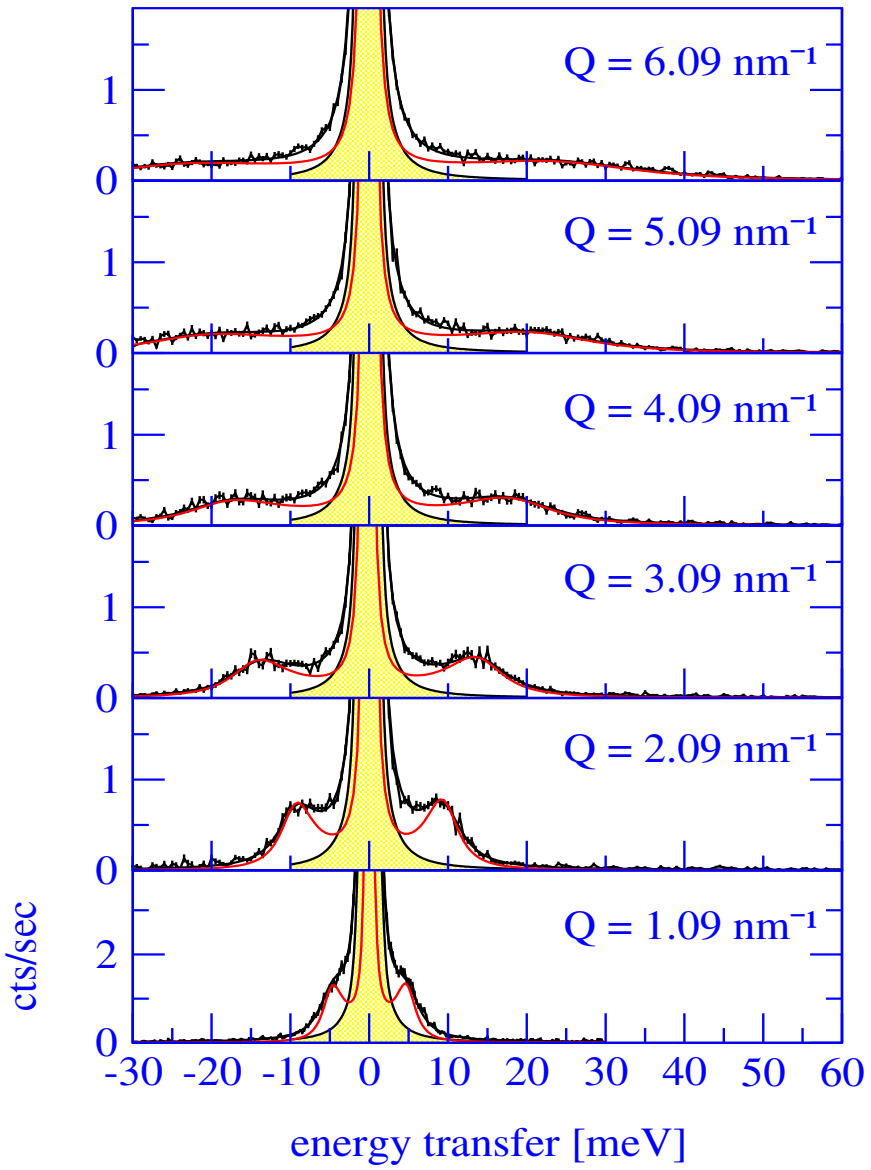


Levitated alumina droplet at APS, 3-ID

Hydrodynamics: 3 peaks

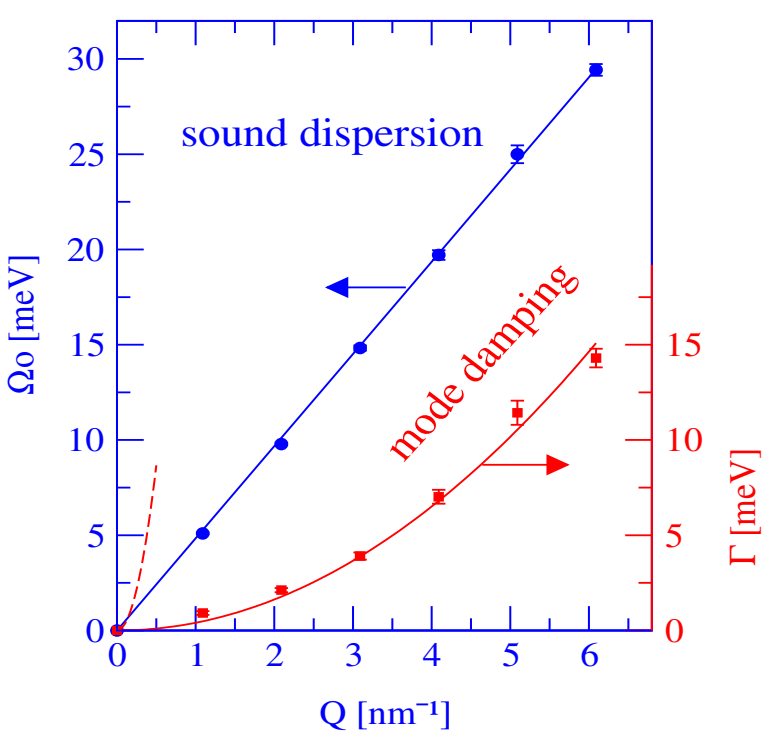


Liquid alumina @ 2400 K

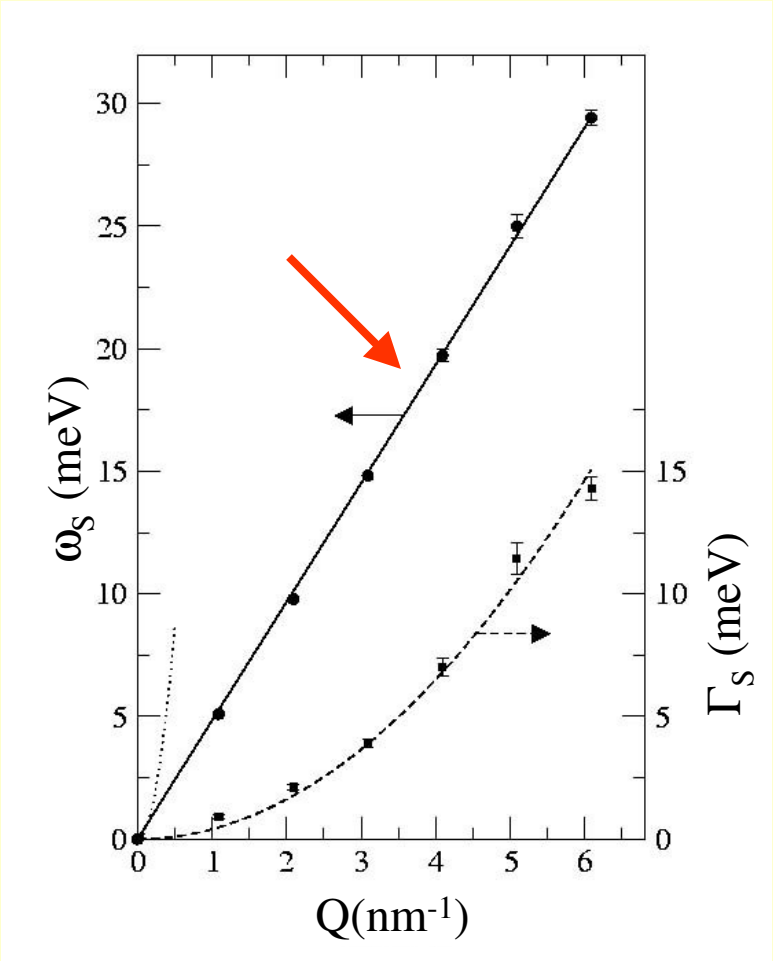


Speed of sound is extracted from Q-dependence of the peak energy, Ω_0

The **mode damping** is related to the widths of the central and the side peaks. The damping of the sound mode $\propto Q^2$ points to a Q-independent underlying damping process.



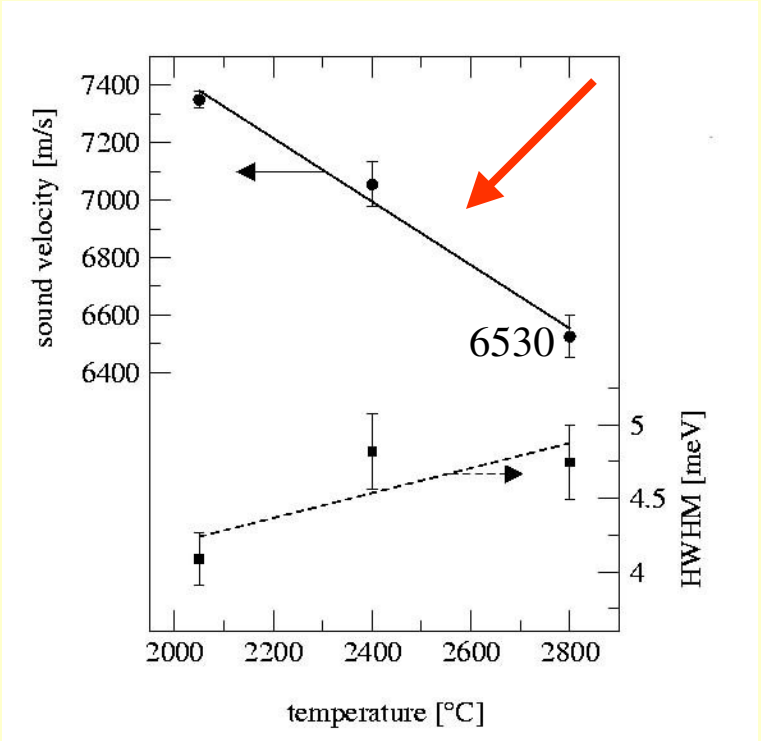
Microscopic sound velocity



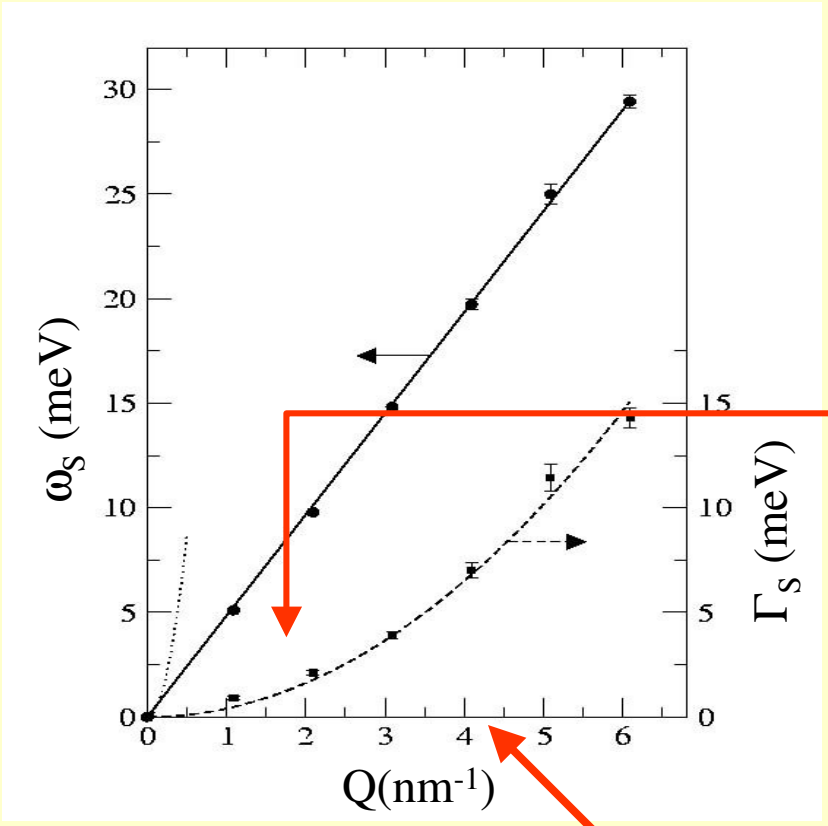
$\omega_S = 4.84Q$

$\vartheta_S = 7350 \pm 60$ m/s

$\vartheta_S \approx 11000$ m/s in the solid



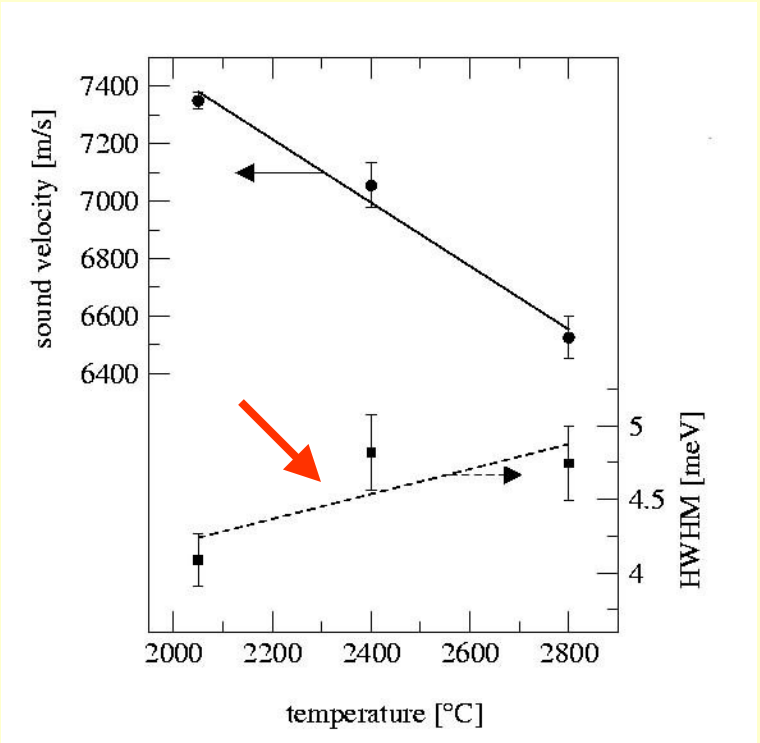
Microscopic viscosity



$\Gamma_S = 0.407 Q^2$

η_l = 4 mPa.s

<< macroscopic value (G. Urbain)



The decrease in the damping of the Brillouin modes as both *Q* and *w* increase beyond the hydrodynamic region is consistent with Maxwell picture of a liquid: at longer times, the system reacts to an external probe with a response time proportional to the viscosity, but at short times with an instantaneous response dominated by the interatomic forces, as if it were a solid.

Phenomenological approach based on Generalized Hydrodynamics

$$S(Q,\omega) = S(Q)e^{\frac{\hbar\omega}{2kT}} \frac{1}{\pi} \mathrm{Re}\left[i\omega + \frac{kTQ^2/MS(Q)}{i\omega + K(Q,\omega)} \right]^{-1}$$

In the hydrodynamic limit $K(Q,\omega) = \frac{\eta_l}{d} Q^2 + K_T(Q,\omega)$

(η_l is the longitudinal viscosity $(4/3\eta+\zeta)$, $K_T(Q,\omega)$ represents the thermal relaxation process)

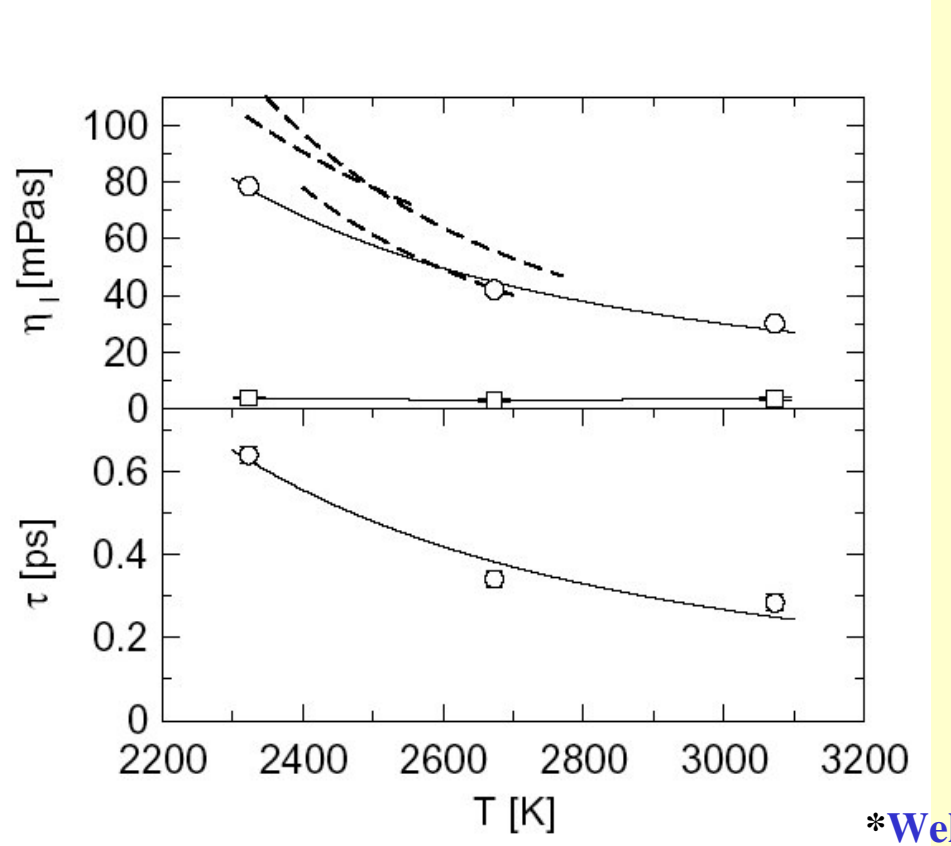
Replacing η_l with frequency-dept. viscosity and neglecting K_T,

$$\eta_l(\omega) = \frac{\eta_l}{1 - i\omega\tau} + \eta_\infty$$

*Spectra up to 6 Å^{-1} can be fitted by same set of (η_l, τ and η_∞)

*η_l, τ exhibit an Arrhenius behavior while η_∞ is approx. constant

Results of fits with a frequency-dependent viscosity



[H. Sinn *et al.*, Science (2003)]

o fits to AXS spectra

□values for η_∞

____ Arrhenius fits

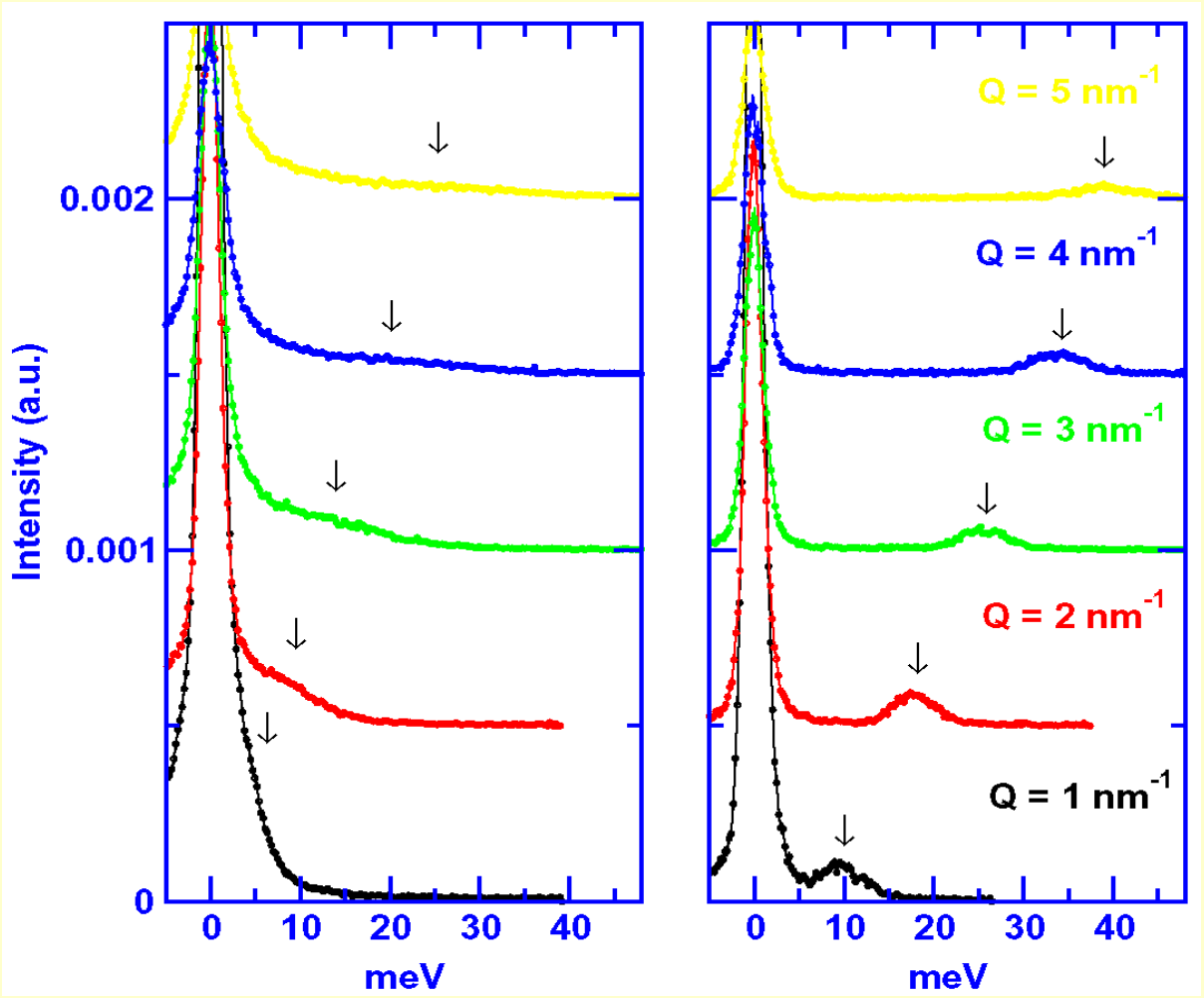
----- 7/3 η from macroscopic data

***Need a new dynamical theory in this regime!**

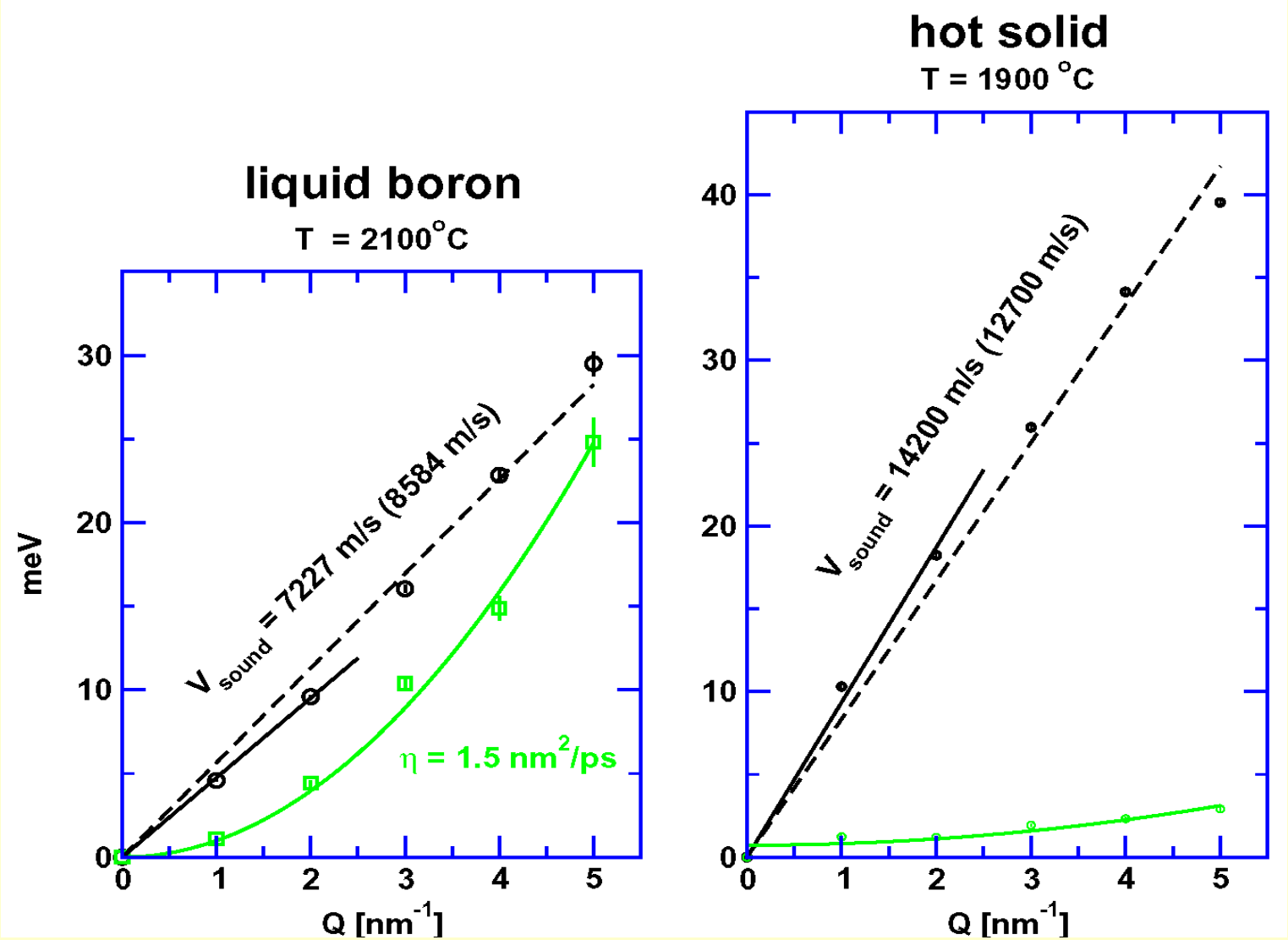
Well-defined triplet structure in *S(Q,ω)

***Clear separation at low *Q* between sound modes and non-propagating density fluctuations**
but: *physical processes are markedly different from hydrodynamic regime*

Boron S(Q,ω)


T =2100°C
T =1900°C (solid)
Intensity (a.u.)
0.002
0.001
0
0
10
20
30
40
meV
Q = 5 nm-1
Q = 4 nm-1
Q = 3 nm-1
Q = 2 nm-1
Q = 1 nm-1

Sound dispersion



Literature:
16000 m/s

Thanks to my collaborators on this work:

M.-L. Saboungi	CRMD, Orleans, France
L. Hennet, A. Bytchkov	CNRS-CRMHT, Orleans, France
E. E. Alp, H. Sinn, A. Atalas	APS, Argonne National Laboratory, Argonne, USA
S. Jahn	GFZ Potsdam, Germany
N. Jakse	University of Metz-LTMC, France
S. Krishnan	Containerless Research, Evanston, USA
P. A. Madden	University of Edinburgh, Scotland
A. Pasturel	CNRS-LPMMC, Grenoble, France ….

appreciation to DOE and CNRS for the funding that made it possible ….

and wishes to Jack and Mike for a

long, happy and prosperous retirement!